Application of Radiation-Induced Graft Polymerization for Modification Polymeric Materials.

Nadezhda Shtanko[1,2]

[1]Dyeing Technology Center, Taegu, Korea

[2]Flerov Laboratory of Nuclear Reactions,

Joint Institute for Nuclear Research,

141980 Dubna, Russia

Introduction.

Radiation-induced graft polymerization is one of the promising methods for obtaining materials with new properties. The modification of polymers by radiation-induced graft polymerization was started over 40 years ago (Chapiro[1], 1957; Charlesby and Pinner[2], 1957; Henglen and Schnabel[3], 1957; Restaino and Reed[4], 1959). The classical monographs by Chapiro[5] (1962) and Charlesby[6] (1960) stimulated these investigations all over the word.

In practice, the radiation-chemical method of initiation is often an easier method for preparing graft co-polymer than the usual chemical method.

The radiation-induced graft polymerization usually is used for modification polymeric membranes to obtain the hydrophilic, ion exchange membranes and membranes with control permeability. The use of radiation-induced graft polymerization is very important for preparation medical haemocompatible polymers and also for modification textile materials and polymeric fibers[7].

The attempts to apply radiation-induced graft polymerization in the textile industry have been undertaken for many years. It was established that radiation-induced grafting made it possible to regulate hydrophilic - hydrophobic properties of fabrics, increased their wear resistance, fire resistance, moisture absorbency and dyeability.

Among of the other using of this method the most important is obtaining sorbents for sorption of transition metal ions from aqueous solutions. Radiation-induced graft polymerization was used for the resolve of various problems: obtaining polymers with catalytic active centers, modification of leathers, inorganic substances, rubbers as well as some kinds of cellulose products.

The highly universal character of this method enables one to perform grafting on practically all known polymers as well as on industrial products made of polymers. This method is universal because it can be used to generate any active center and to prepare desired combination of polymers and polymer materials for any substrate. Note the radiation - induced graft polymerization is suitable for modification of not only radiation-resistance materials, but also materials with low radiation resistance because the radiation dose is easy to vary.

1. Sources of ionizing radiation used in the radiation-induced graft polymerization.

From different kinds of ionizing radiation only γ - rays and electron beam have a practical importance for grafting. In the radiation chemistry of polymers, ^{60}Co and, less frequently ^{137}Cs are used as radiation sources.

The electron accelerators are being successfully used in the radiation chemistry of polymers. An advantage of electron accelerators is their lower radiation danger (when they are switched of, they are radiation-safe). The power and geometry of the beam and the energy and intensity of current of electron radiation can be controlled over a wide range. The current of an electron beam determines the absorbed dose rate. The main limitation of using electron accelerators is the small length of the electron path in condensed media: about 0.5 cm/MeV (Table 1). So, they are suitable for carrying out processes in thin layers.

Table 1. Penetration ability of γ-irradiation and the path of electron radiation

Radiation	Energy (MeV)	Layer of half-weakening of γ-irradiation or mean linear path of electrons in water (cm).
γ- ^{60}Co	1.17 and 1.33	11
γ- ^{137}Cs	0.67	7.5
Electrons	1	0.55
	2	1.0
	3	1.5

Electron accelerators are classified as follows:

1. By the method of energy transfer:

a) direct action accelerators,

b) indirect action accelerators.

2. By the geometry of the electron trajectory (For indirect action accelerators):

a) linear accelerators,

b) cyclic accelerators.

3. By the time relationships of the beam current:

a)   Low energy accelerators (less than 300 keV);

b)   Medium energy accelerators (from 300 keV to 4 MeV);

c)   High energy accelerators (higher than 4 MeV).

4. By the field of application:

a)   research accelerators,

b)   industrial accelerators.

Among indirect action accelerators based on indirect methods of particle acceleration, linear accelerators are more preferred. They are characterized by a high current of the accelerated particles, and

hence by a very high radiation intensity. These accelerators are used for the sterilization of health-care products and the vulcanization of rubber articles of complex configuration. They are also used in the investigation of the radiation resistance of polymer materials and for carrying out and investigating degradation processes.

In radiation - chemical technology, electron accelerators with low energy are mainly used for radiation-induced graft polymerization. It should be noted that radiation-induced grafting requires comparatively low irradiation dose (10-30 kGy as a rule and 100-150 kGy in industry).

2. Methods of graft co-polymerization.

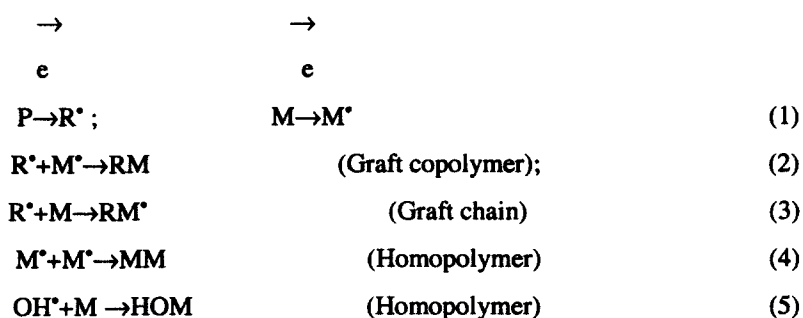We know two types of graft polymerization methods:

1. A direct method.
2. Preirradiation method.

A direct method is the simultaneous irradiation of a polymer and a monomer, or of a polymer swollen in a monomer. Direct grafting gives a high radiation-chemical yield, but simultaneous formation of a homopolymer leads to undesirable consumption of the monomer. In order to suppress homopolymerization, small amounts of metallic salts are added to the monomer solution in which the polymer undergoes swelling.

In the preirradiation method the polymer is first subjected to irradiation and grafting is started by contacting the irradiated polymer and the monomer in the liquid or the gas phase. The process is carried out under vacuum, in an inert medium or in air.

Direct method and preirradiation method in air from liquid phase are mainly used for modification different kinds of polymer.
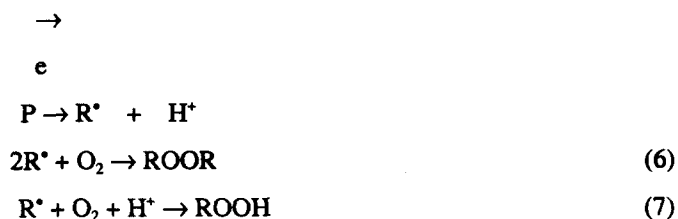
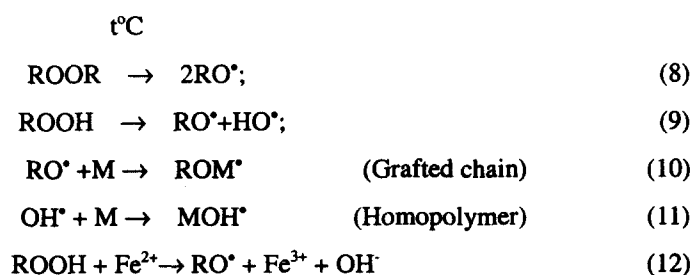The schematic mechanism of reactions for direct method is as follows.

$$\xrightarrow{e} \qquad \xrightarrow{e}$$

$$P \rightarrow R^{\bullet} ; \qquad M \rightarrow M^{\bullet} \qquad (1)$$

$$R^{\bullet} + M^{\bullet} \rightarrow RM \qquad \text{(Graft copolymer);} \qquad (2)$$

$$R^{\bullet} + M \rightarrow RM^{\bullet} \qquad \text{(Graft chain)} \qquad (3)$$

$$M^{\bullet} + M^{\bullet} \rightarrow MM \qquad \text{(Homopolymer)} \qquad (4)$$

$$OH^{\bullet} + M \rightarrow HOM \qquad \text{(Homopolymer)} \qquad (5)$$

Electrons or γ - rays produce radical sites on the polymer backbone and on the monomer (1). As a result of their interactions grafted copolymer is formed (2). At the same time homopolymerization is initiated either by the recombination of monomer macroradicals (4) or by H$^{\bullet}$ and OH$^{\bullet}$ (5) radicals formed from radiolysis of the solvent.

In the method of preirradiation in air free radicals contact with O_2. As a result we have peroxides (6) and hydroperoxides (7).

1. Initiation

$$\xrightarrow{\text{e}}$$

$$P \to R^{\bullet} + H^{+}$$

$$2R^{\bullet} + O_2 \to ROOR \qquad (6)$$

$$R^{\bullet} + O_2 + H^{+} \to ROOH \qquad (7)$$

2. Grafting:

$$t^{\circ}C$$

$$ROOR \xrightarrow{} 2RO^{\bullet}; \qquad (8)$$

$$ROOH \xrightarrow{} RO^{\bullet}+HO^{\bullet}; \qquad (9)$$

$$RO^{\bullet}+M \xrightarrow{} ROM^{\bullet} \qquad \text{(Grafted chain)} \qquad (10)$$

$$OH^{\bullet} + M \xrightarrow{} MOH^{\bullet} \qquad \text{(Homopolymer)} \qquad (11)$$

$$ROOH + Fe^{2+} \to RO^{\bullet} + Fe^{3+} + OH^{-} \qquad (12)$$

When the irradiated polymer is heated in the presence of monomer, the peroxides decompose to give $RO^{\bullet}$ radicals (8), that served as active sites for grafting reactions (10).

The dissociation of the hydroperoxide leads to an equal number of $RO^{\bullet}$ and $HO^{\bullet}$ radicals (9). The $HO^{\bullet}$ radicals are the direct cause of homopolymerization (11). The homopolymer can be reduced in the presence of a metallic salt such as Fe^{2+}. Fe^{2+} converted $HO^{\bullet}$ radicals to the inactive HO^{-}, which can prevent an undesirable homopolymerization (12).

3. Application of radiation-induced graft polymerization for modification of polymer track membranes.

One of the important applications of radiation-induced graft polymerization is modification polymer track membranes by different monomers. In Flerov Laboratory of Nuclear Reactions at Joint Institute for Nuclear Research in Dubna up to now the technique of manufacturing nuclear track membranes from several kinds of polymers has been developed. These membranes are prepared by irradiation of polymer films with accelerated heavy ions followed by etching. By choosing appropriate conditions for irradiation and etching it is possible to prepare a rather wide assortment of polymer TM, which can be used in biotechnology, medicine, ecology, etc[8]. Modification of polymer track membranes by grafting with different polymers extends the possibilities of their use.

The aim of this work was to prepare hydrophilic and thermosensitive track membranes by grafting with the widely used hydrophilic polymer poly(2-methyl-5-vinylpyridine) (PMVP) and with a

"smart" thermosensitive polymer poly(N-isopropylacrylamide) (poly-NIPAA).

3.1. Experimental

Track membranes used in this work were prepared from Melinex biaxially oriented PET-based film (ICI,USA) and Torayfan PP-based film (Topay, Japan).

Radiation-induced graft polymerization was performed using pre-irradiation of track membranes either in air (the peroxide method) or in *vacuo*, as well as by direct method. γ-Radiation of the ^{60}Co and ^{137}Cs isotopes was used. The degree of grafting was determined with respect to the weight of the initial film after through washing of the homopolymer.

Hydrophilic properties of the surface of track membranes were assessed from the results of wetting angle measurements by the sessile drop method using an optical microscope.

Temperature sensitivity of track membranes grafted with poly-NIPAA was determined conductometrically; this method is based on registration of temperature changes in the electrical resistance of a membrane impregnated with the electrolyte (KCl) solution.

The surface of modified track membranes grafted with poly-NIPAA was studied using an atomic force microscope (Nanotechnology-MDT, Russian Federation).

3.2. Results and Discussion

The kinetic curves of graft polymerization have a typical shape with "saturation" (Fig. 1). Such a behavior of the curves is explained by progressive conversion of the active centers of graft polymerization with time, especially in thin polymer films. It is noteworthy that the rate of graft polymerization of MVP is much higher than that of NIPAA. This can be explained both by higher diffusion rate and increased swelling of PET in MVP compared to the analogous characteristics of the process in NIPAA which has larger molecules. Mention should also be made of higher MVP sorption on the surface of track membranes due to complexation between the nitrogen atoms of the pyridine rings of MVP and carboxylic groups formed in track membranes in the course of preparation. This results in activation of the monomer and in an increase in the polymerization rate[9]. Increased decomposition of peroxide groups, which are generated in track membranes exposed to irradiation in air, during their interaction with the pyridine bases of the MVP molecule also plays an important role[10]. Irradiation of PET track membranes in *vacuo* is responsible for the higher initial rates and limiting degrees of grafting, which is explained by the fact that the graft polymerization proceeds involving free radicals generated immediately upon irradiation of PET[11]. Noteworthy is also that, at nearly the same porosity values, the initial rate of graft polymerization and the limiting degree of grafting decrease linearly as the pore diameter decreases (Fig.2).
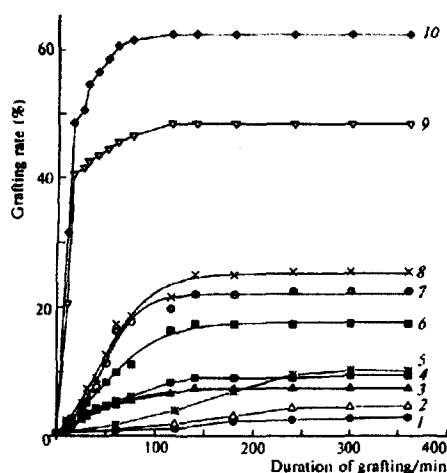
Fig.1. Kinetic curves of post-graft polymerization of MVP and NIPAA onto the surface of PET- and PP-based track membranes. Dependence of the yield of PMVP grafted at 70 °C onto the surface of PET-based (3,4,6,7,9,10) and PP-based (8) membranes and that of poly-NIPAA (1,2,5) grafted at 45°C onto the surface of PET-based track membranes (at concentration of Mohr's salt of 0.025%; post-grafting on track membranes irradiated in air) on the duration of the process: the peroxide method (1-8), irradiation dose/kGy: 180 (1-7) and 10 (8); and the method of preirradiation in *vacuo* (9,10) at an irradiation dose of 50 kGy and at dose rate of 0.85 Gy s^{-1}. Pore diameter/µm: 0.03 (1); 0.05 (2, 4); 0.04 (3);).1 (5, 6, 9); 0.2 (7); 0.3 (8) and 1.0 (10).
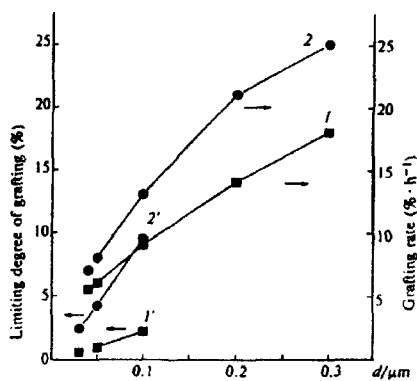
Fig.2. Dependence of the rate of graft polymerization (1, 2) and limiting degree of grafting (1´, 2´) of poly-NIPAA (1, 1´) and PMVP (2, 2´) onto the surface of track membranes by the peroxide method on the pore diameter (d) of track membranes.

This can be explained by the fact that effective surface of track membranes increases as both the pore diameter decreases and the number of pores increases and, hence, by the increase in defectiveness of the membrane material. Under these conditions, a radical recombination reaction is favored, thus

- 10 -

decreasing the concentration of the active centers initiating the graft polymerization[12].

Studies of gas permeability of the graft-modified membranes showed that it decreases as the degree of grafting increases (Fig.3). A substantial decrease in the gas permeability and gasdynamic pore diameter is observed after the degree of grafting exceeds a particular threshold (Figs. 3, 4, 5).
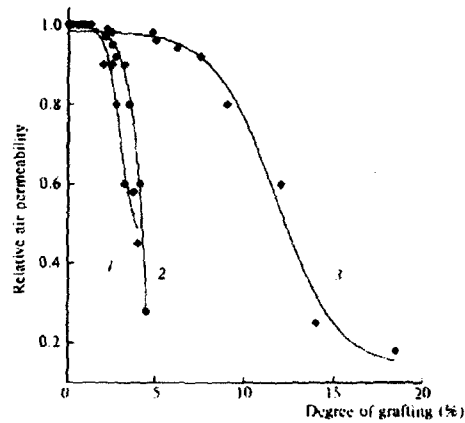

Fig.3. Dependence of relative air permeability of PET-based (1, 2) and PP-based track membranes (3) on the degree of grafting of PMVP. Pore diameter/μm: 0.04 (1); 0.05 (2) and 0.3 (3).
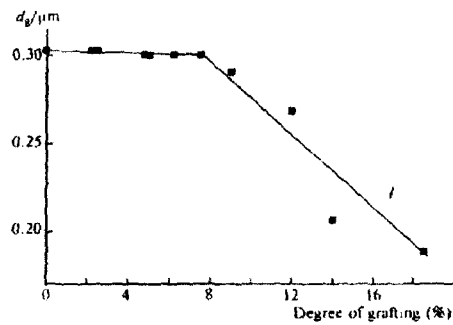
Fig. 4.
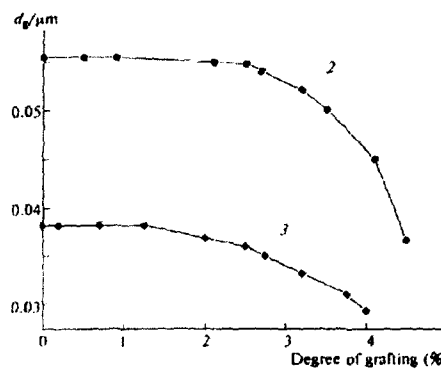
Fig.5.

Fig.4, 5. Dependence of gasdynamic pore diameter (d_g) of PP-based (1) and PET-based (2, 3) membranes on the degree of grafting. Initial pore diameter/μm: 0.3 (1); 0.05 (2) and 0.04 (3).

An increase in hydrophilicity of track membranes with increasing degree of grafting leads to a decrease in the wetting angle (Fig.6). Hydrophilic properties are stabilized at a grafting value of 5-7% due to the coverage of the surface layer with grafted PMVP chains. Analogous physical effects have also been observed in studies of other grafted systems[13].
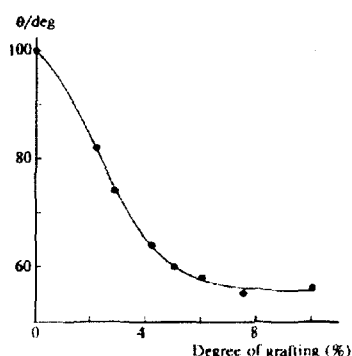

Fig.6. Dependence of the wetting angle (θ) on the degree of grafting of PMVP for PP-based track membranes with a pore diameter of 0.3 μm.

The dependence of water permeability of the graft-modified membranes on the degree of grafting passes through a maximum (Fig.7), whose position is shifted towards greater degrees of grafting as the pore size increases. We established that at the optimum content of grafted PMVP, the water permeability of hydrophilic small-pore PET-based track membranes increases by a factor of 3-4 as compared to that of initial membranes (see Fig.7). A clearly seen correlation is observed between the dependence of gasdynamic pore diameter and water permeability on the degree of grafting (cf. Figs. 4, 5 and 7).

The maximum value of water permeability is achieved at such degrees of grafting that correspond to virtually unchanged gasdynamic pore diameter. The range of grafting values at which the pore diameter decreases (see Fig.4, 5) corresponds to the region of drastic decrease in water permeability (see Fig. 7). Thus modification of the properties involves two stages. The characteristics of the first stage are insignificant changes in the geometric parameters of pores and pronounced changes in the surface properties (wetting). This imparts the desired hydrophilic properties and increased water permeability to the membrane. According to the data of wetting angle measurements (see Fig. 6), the maximum value of water permeability corresponds to the highest hydrophilicity. The second stage is characterized by marked changes in geometric parameters of the membrane and degradation of its service properties. It should be noted that the numerical values of the parameters characterizing transfer of liquid through modified membranes remain unchanged on storage of the track membranes under standard conditions over more than a year.

We also studied grafting of track membranes with poly-NIPAA. A characteristic of this polymer is the existence of a lower critical solution temperature in aqueous solution. At 32°C, phase transition of the
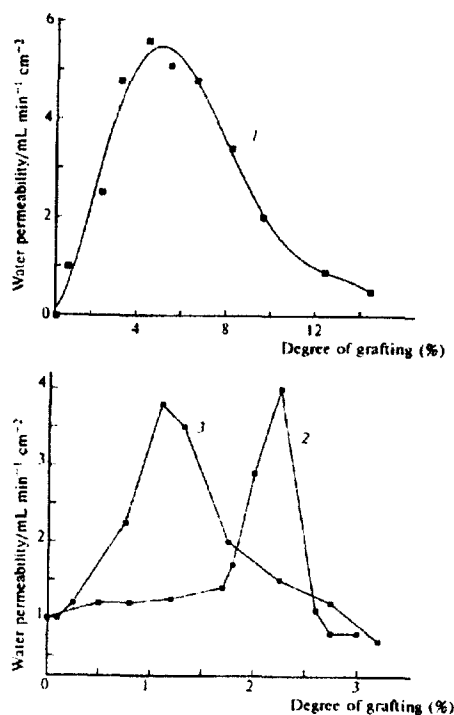
Fig.7. Dependence of water permeability of PP-based (1) and PET-based (2, 3) track membranes on the degree of grafting of PMVP. Pore diameter/μm: 1 - 0.3; 2 - 0.05 and 3 - 0.04 (ΔP=0.07 MPa). For clarity, the plots are shifted along the ordinate axis.

polymer occurs, caused by conformational transition of macromolecule from a loose coil to a compact globule. This transformation is due to the increasing role of hydrophobic interaction with increase in temperature[14]. Hence it could be expected that the parameters of track membranes grafted with poly-NIPAA are temperature dependent. In this connection, we carried out a conductometric study of temperature sensitivity of track membranes grafted with poly-NIPAA. The conductivity of initial PET-based track membrane is a linear function of temperature both on heating and on cooling. The conductivity of PET-based track membranes grafted with poly-NIPAA increases substantially in the temperature range 32-34°C on heating and decreases drastically in the same temperature range on cooling (Fig. 8). This temperature range corresponds to the phase transition temperature of poly-NIPAA, at which the size of macromolecules constituting the polymer decreases appreciably. The reverse is observed on cooling.

Investigation of water filtration through PET-based track membranes grafted with poly-NIPAA in the temperature range 20 - 45°C revealed a substantial increase in water permeability at temperatures between 30 and 34°C (Fig.9), which corresponds to the phase transition temperature.
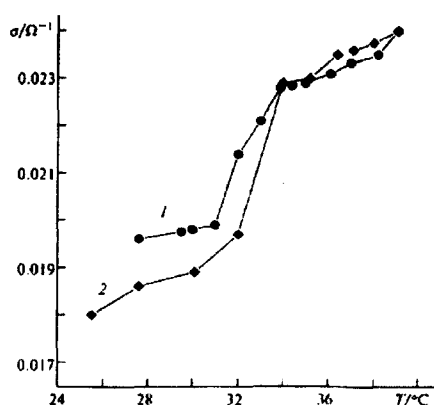
Fig.8. Dependence of conductivity (σ) of PET-based membrane grafted with poly-NIPAA on the temperature (T) of the medium: cooling (1) and heating (2). Conditions: degree of grafting , 5.6%; pore diameter, 1 μm; L=20 μm; N=4.6x10^5 cm^{-2}.
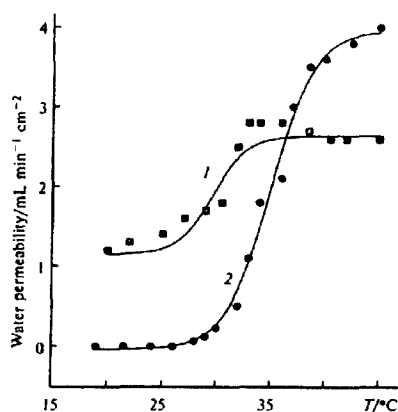

Fig.9. Dependence of water permeability of track membranes grafted with poly-NIPAA on the temperature (T) of the medium. Conditions: ΔP = 0.07 MPa, L = 10 μm and N= 1.5x10^6 cm^{-2}. Degree of grafting (%): 3.4 (1) and 7.5 (2).

The structure of modified membranes was studied by scanning electron microscopy. Radiation-induced grafting with NIPAA leads to changes in the structure of track membranes surface (Fig.10), which becomes more regular (see Fig. 10, b, d). This is not observed for the initial PET-based membrane. The pore size decreases due to the increase in the thickness of the grafted layer covering the walls of cylindrical openings (see Fig.10, d). The near-surface layer of modified membrane has a regular structure, which is different from the layered structure of the initial PET-based membrane. At a grafting value of 12.7 %, the thickness of the graft-modified membrane increases by approximately 2 μm.

a

b

c

d

e

f
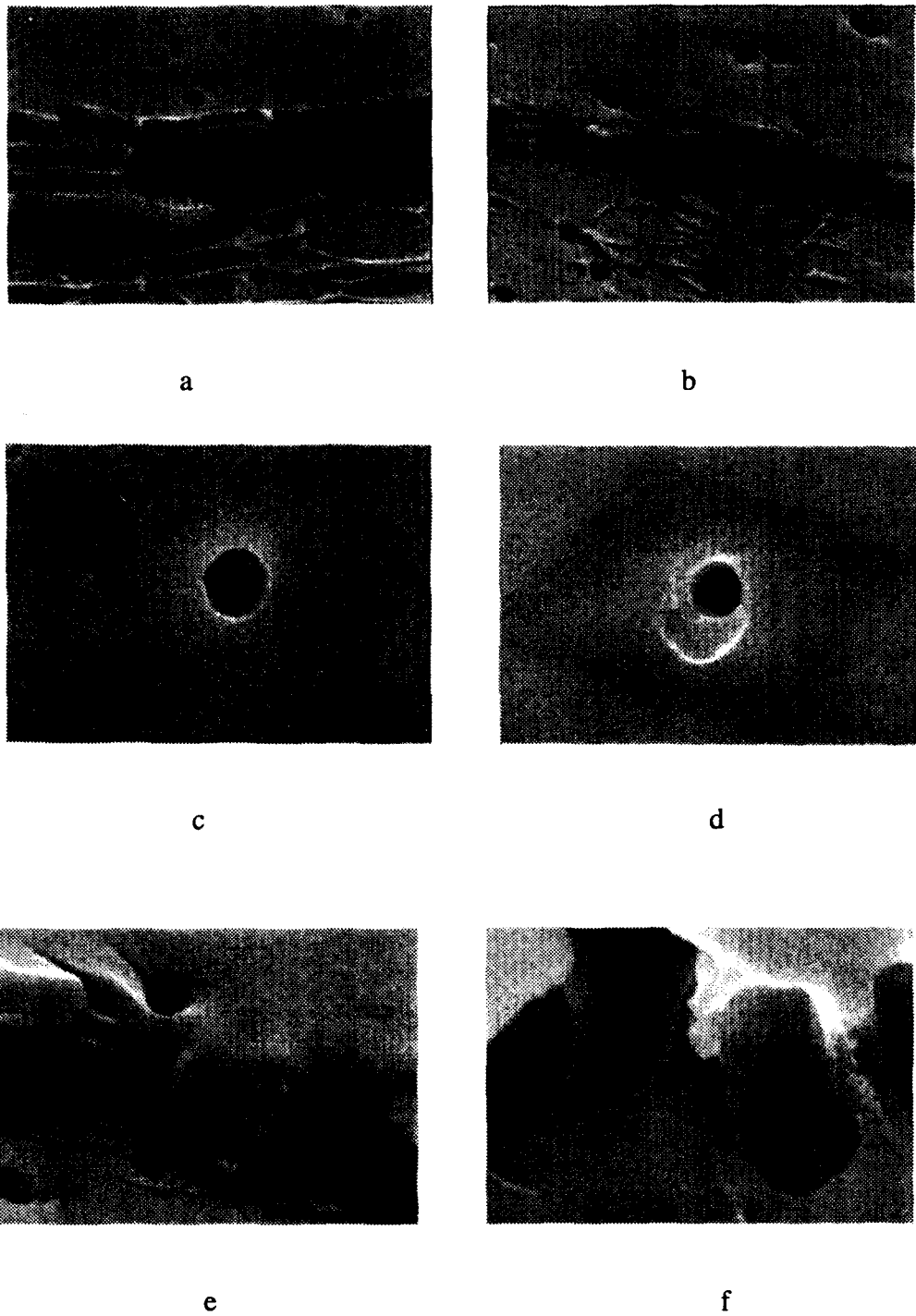
Fig.10. Photomicrographs of PET-based membranes obtained by scanning electron microscope: initial membrane with a pore diameter of 1 μm (a, c) and membrane grafted with poly-NIPAA (b, d - f). The degree of grafting was 12.7 %. Field of vision area/μm^2: 15x11 (a, b); 5x3.8 (c-e); 2.5x1.9 (f).
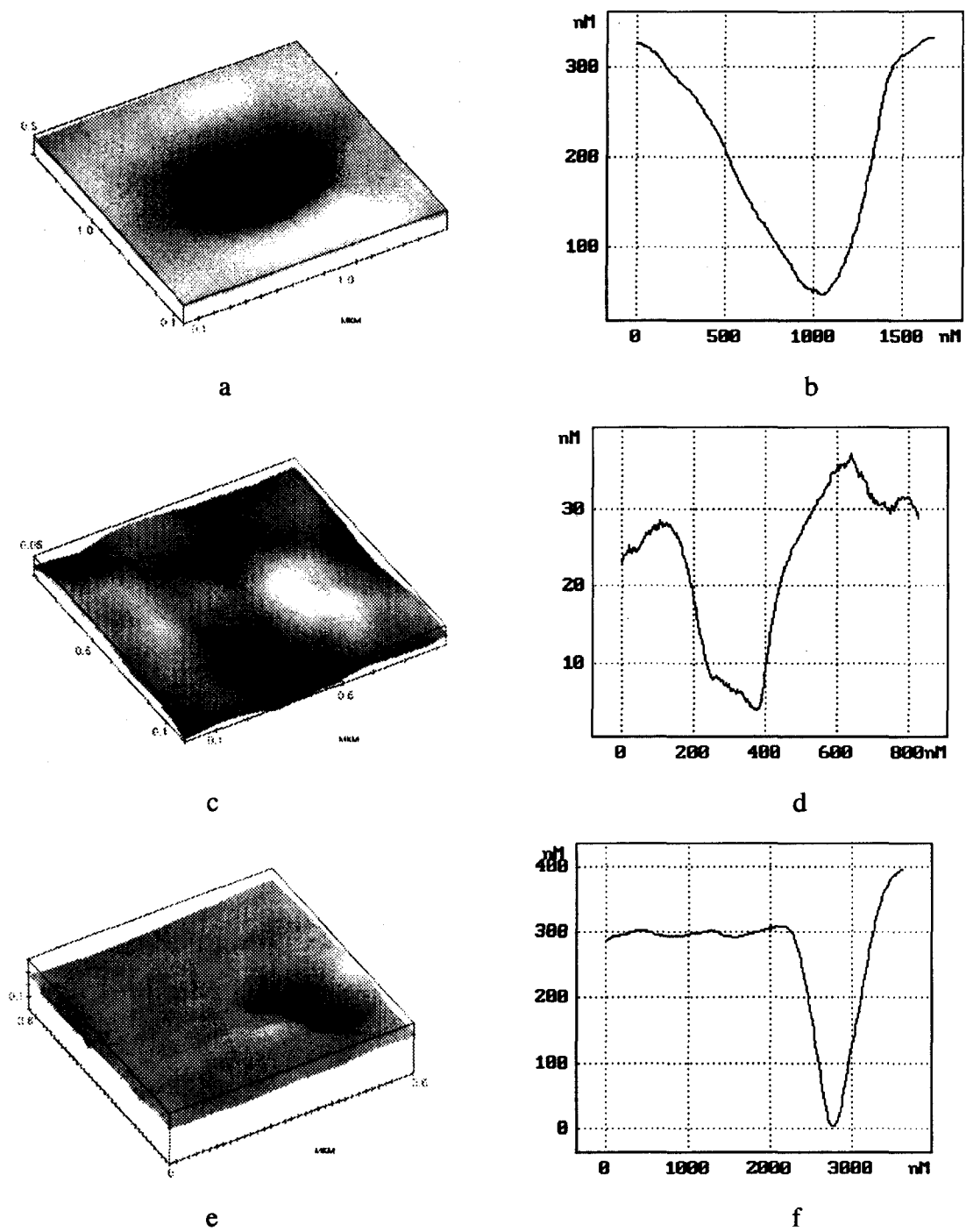
Fig.11. Atomic force microscopy images of PP-based membranes (a, c, e) and profiles of the corresponding membranes (b, d, f): surface of initial membrane with a pore diameter of 0.9 μm (a); surface of membrane grafted with poly-NIPAA (degree of grafting 6.5%) swollen in water at room temperature (c) and kept in water at 50°C for 30 min (e).

As can be clearly seen in the photomicrograph of an individual pore (see Fig.10, d), the near-wall layer of grafted poly-NIPAA is partially destroyed on exposure to an electron beam, which is not observed for the initial PET-based membrane (see Fig.10,c). Not only does the grafted poly-NIPAA cover the membrane surface and the pore walls, but it also penetrates into them to some extent (see Fig. 10,e, f).

Atomic force microscopy images of the surface of track membranes and the corresponding profiles are shown in Fig. 11. On going from Fig. 11, a to Fig. 11, e it is possible to trace the changes in the pore size of the track membranes under study. Swelling of track membranes grafted with poly-NIPAA results in a decrease in the pore size (see Fig.11, c). If track membranes grafted with poly-NIPAA is allowed to stay at elevated temperatures, phase transition occurs and the pores are opened (see Fig. 11, e).

Thus, our study revealed the possibility of application of radiation-induced graft polymerization for preparation of hydrophilic and thermosensitive track membranes. The applications of the radiation-induced graft polymerization for obtaining new materials will be extended in the future.

References

1) Chapiro A. (1957) Industr. Plast. Mod., 9, 34.

2) Charlesby A. and Pinner S.H. (1957) Industr. Plast. Mod., 9, 43.

3) Henglein N. and Schnabel W. (1957) Makromol.Chem. 25, 119.

4) Restaino A.J. and Reed W.H. (1959) J. Polym. Sci. 36, 499.

5) Chapiro A. (1962) Radiation Chemistry of Polymeric Systems. Interscience , New York.

6) Charlesby A. (1960) Atomic Radiation and Polymers. Pergamon Press. Oxford.

7) V.A. Kabanov, R.E.Aliev and Val. N. Kudryavtsev (1991) Radiat. Phys. Chem., v. 37, 2, p. 175-192.

8) P. Yu. Apel, A.Yu. Didyk, N.I. Zhitariyuk, I.E.Larionova, T.I.Mamonova, O.L. Orelovitch, L.I. Samoilova and I. Yanina (1994) Russian Colloid J., 56, 746.

9) V.A. Kabanov and D.A. Topchiev (1975)Polymerization of Ionizing Monomers, Nauka, Moscow, 108, in Russia.

10) E.T. Denisov and V.V. Azatyan (1997) Inhibition of Chain Reactions. Russian Academy of Sciences, Chernogolovka, 81 (in Russia).

11) B.L. Tsetlin, I.Yu. Babkin, V.Ya. Kabanov and A.N. Ponomarev (1985) High Energy Chemistry, 19, 303.

12) Radiation stability of Organic Materials, Eds.V.K. Milinchuk and V.I.Tupikov (1986) Energoatomizdat, Moscow, 30 (in Russian).

13) V.M. Rudoi, L.P. Sidorova and V. Ya. Kabanov (1988) Polymer Science, A, 30.

14) E.I. Tictopula, V.N. Uversky, V.B. Lushchik, S.I. Klenin, V.B. Bychkova and O.B. Ptitsyn (1995) Macromolecules, 28, 7519.